

Rocky Flats Environmental Technology Site. Actinide Migration Evaluation
Meetings April 18-19, 2000
Advisory Group Greg Choppin, David Clark, David Janecky, Kirk Nordstrom

Summary and recommendations for path forward

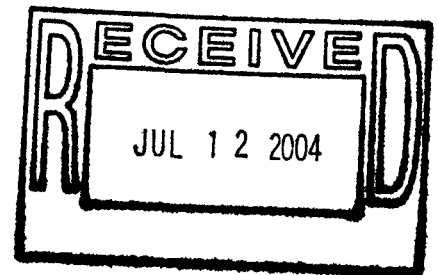
Areas of discussion during this meeting of the AME advisory group included the status and reorganization of the Rocky Flats Environmental Management projects, colloid transport studies, the on-site rangeland burn, design of the pathway analysis report, spectroscopic investigation of Pu speciation in concrete, uranium geochemical modeling, responses to comments on actinide migration reports and the present status of data quality objective definitions. In addition, we continued discussion of recent technical publications on actinide colloid transport and Pu phases in response to questions at the public meeting.

Several recommendations were identified in advisory group discussions, based on this range and scope of actinide migration evaluations. The advisors have identified the importance and opportunity to sample the subsurface source region for U in solar ponds and to move forward in integration of U isotopic data with modeling of geochemistry and water balance. At upcoming meetings, it will be important to hear more discussion on the Industrial Area and rebaselining progress and decisions.

Progress and integration

The initiation of concrete spectroscopy studies of Pu speciation has been a great success. Continued support of these difficult measurements is of key importance to success in actinide migration evaluation for Rocky Flats.

A variety of activities were presented, and the diversity and integration of these activities is filling gaps and providing valuable constraints on the whole site (targeted on getting to 2006 and providing a strong basis for stewardship activities).



Results and Discussions

RFETS current status of site projects and reorganization – Dave Shelton

The closure activities at RFETS are at an important juncture in the sense that the pressure to meet the 2006 deadline is keenly felt and activities must be clearly focused, efficient, and relevant. Obvious data gaps in information must be identified and the information obtained in the most expeditious manner. Research studies will still be necessary but these studies must be kept focused on those issues that are required for safe and appropriate closure of the site. DOE and Kaiser-Hill have done a credible and laudable effort at obtaining data and improving their understanding of site characteristics and processes to improve the success of site closure. Such effort must be continued during this final stage towards closure.

As the approach to closure continues and Kaiser-Hill looks forward to completion of its responsibilities, it becomes essential to consider the long-term responsibilities of DOE beyond 2006. These long-term considerations, or future stewardship, must be formulated into a plan that fits smoothly with the near-term closure activities. Development of such a plan will be a key ingredient to future land use and to the environmental concerns of the surrounding communities.

Colloid Transport – Peter Santschi -

The studies at Texas A&M University have confirmed further that Pu and Am in the RFETS environment migrate via transport by colloidal and particulate species with an insignificant role for species at the ionic/molecular level. A significant finding was that humic acids present in the waters can cause disaggregation to smaller particles, while polysaccharides promote aggregation to larger particles.

These basic studies are useful as they confirm other data which was best interpreted as colloidal/particulate transport and have also given valuable insight into the differing roles of major natural organics. This project continues to give important insights and greater understanding of the major general factors involved in Pu/Am transport at RFETS, and we are looking forward to seeing field and laboratory results from this year's work.

On-Site Rangeland Burn – Bob Nininger

Preliminary results were presented from the long-planned rangeland test burn. The original plan called for a controlled burn of 500 acres in the buffer zone to improve the survival of native vegetation and to collect valuable data pertaining to the air transport and resuspension of radionuclides, especially for wildfire scenarios. About a 50 acre subplot was burned as a test for feasibility and to determine adequacy of procedures. Wind velocity and direction was measured at regular and short intervals, soil temperature was monitored as the burn front passed through and radioactivity (α and β counts and Pu isotopic determinations) was measured in soils, vegetation, and in air. Air monitoring was

done before and during the burn from three collectors (one upwind and two downwind) Soils and vegetation in areas to be burned were also sampled for radioactivity levels A wind tunnel was set up on site to measure particle transport and resuspension rates

Near the beginning of the burn, the wind direction quickly changed by nearly 180° but the locations of the collectors still allowed for adequate recovery of airborne particulates A couple of hours later the wind direction changed again Wind velocities were all within a manageable range for the collectors Surface soil temperatures reached a maximum of 193°C during a minute or two as the burn front passed through (presentation by Pat Haines) The analytical determinations have not been completed so only a small portion of the data is available Results for soil radioactivity showed very uniform and low levels of α and β activity characteristic of background The preliminary results indicate the test burn was a success and the complete burn should also be a success

Pathway Analysis Report outline – Ian Paton & Rob Smith

In general, this outline provided and described in the presentation indicated that this report should be quite useful in completion of operations leading to remediation and closure, especially by linkage to the conceptual model report and document hierarchy The topics listed are those of primary interest and the scope seems to sufficiently broad yet with proper detail to result in a valuable document In Section 2.0, it would seem important to emphasize that Pu/Am migrate via colloidal/particulate transport, whereas U migrates as an ionic/molecular complex As a result, very different models must be employed for Pu/Am vs U transport evaluations

In the Technical Appendix, a section (2.5) is to be devoted to the use (and limitations) of use of empirical Kd values in modeling calculations It is important that the use/limitations discussion treat Pu/Am and U separately Use of Kd values in modeling ionic/molecular species (i.e. U) has more, though still limited, value However, use of Kd to model the behavior of Pu/Am forming or sorbed to particulates is much more of a concern technically and should be used as a last resort as reproducibility, applicability to different media and over various conditions are major unknowns or limitations and require much more investigation of the limitations, etc prior to application decisions

Concrete spectroscopy preliminary results and issues – Pat Ervin

During February, PuO₂, and Pu(VI) hydroxide and carbonate standards, and concrete samples spiked with these same standards were analyzed by X-ray Absorption Fine Structure (XAFS) spectroscopy Analysis of the data clearly shows that one can differentiate between Pu(IV) and Pu(VI), and the identification of PuO₂ in spiked concrete was clear Unfortunately, no Pu was observed in many of the target concrete samples containing Pu At this time it is unclear whether this represents a heterogeneous sample or a detection

threshold In view of the success of this technique in identifying PuO₂ in soils (also a very difficult analysis that took several tries), the team is encouraged to keep trying during their scheduled experimental run in June

DQO Update – Mike Peters

Major revisions have been made to the original 1998 DQO document An air component has been added, "The Problem" section has been updated, Table 2 has been updated (data needs, availability, and attainability), the study boundaries have been better defined, a section on limits on decision errors has been added, and the limits on uncertainties section is relatively little changed Three important areas for application of DQOs to modeling were identified (1) sensitivity and uncertainty analysis, (2) calibration (comparison of predicted values with measurements), and (3) model verification and validation (assessment of model adequacy) The section in the AME DQO revision 6 on Model Requirements, subsections on sensitivity/uncertainty analysis and on model verification/validation raise certain issues that must be carefully considered These requirements are based on DOE Order 414.1 and cover a lengthy set of useful criteria that, if followed, should result in documenting the utility and applicability of any models used for site characterization and risk assessment

Three practical difficulties arise in the application of these DQOs The first is the semantic problem associated with the use of such words as verification and validation It has been pointed out repeatedly in the literature that scientific models do not lend themselves readily to "truth checks" Indeed, their purpose is not to so much to "reflect, simulate, or represent reality," as to improve our understanding of complex processes and phenomena by constraining or limiting the possibilities Furthermore, these words have been losing their meaning because they have been used and misused for a large variety of purposes Hence, the words verification/validation should be avoided whenever possible The subsection Model Verification/Validation could be retitled "Model Assessment" or "Model Evaluation" Similar problems arise with the phrase "model validation" in the text If model validation has been completed, does it mean that the model in question has been validated? What does this mean?

It is acknowledged in the DQO that "Models have always a limited range of validity, " This statement suggests that models are neither valid nor invalid, creating a further semantic difficulty Indeed, since models are idealized simplifications of reality they could be described as having no range of validity because no model exactly represents reality or they could be described as having any range of validity because goals and purposes are predefined and models can be made to conveniently fit them It is better to state that a model can be evaluated with respect to a reasonable range of conditions required of it for a particular purpose, and avoid the use of "valid," "validity," and "validation" altogether The second difficulty has to do with the extensive list of criteria

offered for sensitivity/uncertainty analysis and for verification/validation. If ALL of these criteria were met, modelers would spend all of their time evaluating a model rather than actually applying it. Reasonable flexibility must be allowed for the degree to which modelers need to evaluate models so that valuable time is not wasted, especially on exercises that are treated adequately in the scientific or engineering literature. The third difficulty is the lack of distinction between evaluating a conceptual model, a mathematical model, and a computer code. Evaluating each of these entities means quite a different task with a different result. Sometimes useful references to the literature are all that are needed whereas other times a series of well-executed computations are needed. Most of the criteria arising from Order 414.1 refer to determining the reliability of a computer code, but the statements in the DQO are not clear on this aspect and should be made so.

Uranium Geochemical Modeling – Jim Ball

Leakage of liquid wastes from the former Solar Evaporation Ponds has produced a contaminant plume characterized by high concentrations of nitrate and uranium. For the uranium plume, important questions have been raised as to the contribution of naturally occurring uranium relative to waste-derived uranium and as to the processes affecting uranium mobility such as mineral solubility control. Uranium isotopes (235, 236, and 238) were measured from a few wells to help identify natural vs. anthropogenic sources. Indications of both depleted and enriched uranium with measurable ^{236}U were obtained from the Solar Ponds Plume whereas background (uncontaminated) wells were found to have non-detectable ^{236}U and natural activity ratios of $^{235}\text{U}/^{238}\text{U}$. However, the sampling was limited in scope, there is still some possibility of natural uranium contributions in the area, and mixtures of depleted and enriched uranium could occur with little or non-detectable ^{236}U to give the appearance of naturally-occurring material. Sampling and isotopic measurements to date have shown clearly that uranium isotope systematics can be used to differentiate natural from anthropogenic uranium sources and that both sources exist at RFETS although the extent of natural source material at Solar Ponds is unclear. Further measurements are currently underway that should reduce this uncertainty.

A geochemical modeling investigation on the potential for mineral solubility control on uranium mobility has shown that ground waters in the Solar Ponds are undersaturated with respect to all U(IV) and U(VI) minerals for which reliable thermodynamic data exist. These results would suggest that uranium should be relatively free to move with the ground water unless some process besides mineral precipitation is slowing or attenuating the transport. The fact that the uranium plume as mapped appears distinctly attenuated compared to the nitrate plume suggests 3 possibilities for attenuation: (1) sorption processes, (2) capillary movement into the vadose zone during dry periods forcing mineral precipitation, and (3) uranium precipitated immediately beneath the Solar Ponds.

as leaking solutions reacted with the aquifer material. The tendency for the highest uranium concentrations to be spatially located close to the Solar Ponds (unlike the nitrate) and the tendency for all the ground waters to be undersaturated with respect to uranium mineral solubilities suggests that the third possibility, uranium precipitation beneath the Solar Ponds and a slow rate of dissolution, is likely. The potential occurrence of elevated uranium in the soils and sediments needs to be determined because it could have a major influence on the remediation activities. It is essential that geochemistry and isotopic information and interpretations are put on a firm spatial basis to further understanding of the Solar Ponds system and to provide a basis for evaluation of other locations of uranium contamination.

Air Model – Response to comments from Whicker and Hakonson – Martha Hyder

An outline was presented that described the detailed response to TRG comments on the report entitled "Air Transport and Deposition of Actinides at the Rocky Flats Environmental Technology Site FY00 Report." Martha Hyder is to be congratulated for her careful and professional responses to each reviewer comment. The strategy is sound, and the responses are detailed and thoughtful, and should go a long way towards improving the TRG's understanding of the strategy, approach, and results of the air modeling.

"Actinide Migration Studies at the Rocky Flats Environmental Technology Site: The Effect of Soil-Water Redox Potential on ^{239,240}Pu Solubility" report by Dr. Honeyman – Response to CAB TRG comments

We agree with the CAB TRG reviewers' summary comments that these experiments have reaffirmed the results of similar studies that date back at least 20 years. The report reflects the technical details of key scoping studies that were implemented in response to process hypotheses and public concerns that developed as a result of actinide mobility measurements at RFETS from the May 1995 storm. This approach was further refined and targeted through discussions among RFETS site personnel, AME external advisors, and stakeholders during the several years that the experiments were done.

The report was not designed as a peer-reviewed publication, or as the complete consideration of actinide migration in soils at RFETS. Rather, this report is a building block to evaluate the importance of these conditions and processes as a component pathway of the conceptual model. A critical focus intended for this work was the need for further work on detailed and robust characterization of specific redox processes that would enhance actinide migration. Given the consistency of the results with previous work and the lack of identification of new processes that contribute to or enhance actinide migration in soils, further investigation of actinide mobilization during soil reducing conditions has been determined not to be a priority.

The AME advisors have recommended that Kaiser-Hill write a summary (e.g. in the Pathway Analysis Report) that places these scoping studies in the context of the conceptual model and site remediation, cleanup and monitoring activities

Erosion Modeling Draft Report – response to comments – Win Chromec & Greg Wetherbee

The report is comprehensive, deals with complex technical issues, and is very long. When modified, edited, polished, and in final form, it will be a landmark document describing analyses of erosion and sediment transport affecting actinide transport and water quality impacts. The authors are to be commended for its depth and thoroughness, its clarity and for their professional approach in presenting modeling results with the associated interpretations and uncertainties. The report consists of two main parts, (i) a summary report presenting an overview and the main findings/conclusions, and (ii) appendices A-D providing details and additional information supporting materials presented in the main report. The report should be read and interpreted in its entirety. This is necessary to gain a perspective of its purposes, findings, scope and limitations. Nonetheless, some readers will focus only on summary statements without analyzing and interpreting the background information supporting the statements and conclusions. Therefore, the authors should carefully review the "Executive Summary", "Introduction", and "Summary, Conclusions, and Uncertainty" sections to make sure that every sentence and every finding and conclusion is supported and explained in detail in the Report.

Further discussion of Pu chemical forms and transport

Most probable chemical forms of Pu in RFETS soils The probability of release of plutonium from RFETS soils to the surrounding environment will be determined by a variety of factors, some of which are currently being addressed by Actinide Migration Evaluation. The fate and transport of plutonium will be governed by the solubility of its compounds in groundwater and surface waters, the tendency of plutonium compounds to be adsorbed onto mineral phases in soil particles, and by the probability that the colloidal forms of plutonium will be filtered out by the soil or rock matrices, or adsorb or settle out during transport.

The solubility of plutonium compounds will depend largely on the oxidation states. As in the case of other polyvalent metal cations, the lower oxidation states of plutonium are more stable in acid solution, and the higher oxidation states are more stable in basic solution. Complexation can alter these generalizations. The greater complexing strength of Pu(IV) causes Pu(III) to be oxidized to Pu(IV) in neutral media.

Generally, plutonium will exist in aqueous solution as Pu(V) and Pu(VI) with Pu(V) predominating in oxidized natural waters. For plutonium in the lower oxidation states (III) and (IV), the solubilities are generally exceedingly low.

Oxidation or reduction of higher oxidation states can lead to the formation of colloidal forms of "Pu(OH)₄" or "PuO₂ · 2H₂O" often referred to as "plutonium hydrous oxide" or "Pu(IV) polymer". Pu(IV) colloids are often kinetically very stable in solution, but eventually tend to be absorbed or filtered out due to interactions with mineral and soil phases. The slow crystallization of Pu(IV) colloids leads to greater stability and lower solubility.

In natural waters plutonium solubility is limited by the formation of amorphous Pu(OH)₄ or polycrystalline PuO₂. A reasonable estimate for the solubility product (K_{sp}) of Pu(OH)₄ is approximately 10⁻⁵⁴. This estimate puts an upper limit on the amount of Pu that can be present, even if Pu(V) or Pu(VI) are the more stable solution forms. Pu(V) has a low tendency to hydrolyze and form complexes with ligands, and is much less likely to be sorbed to solid surfaces and colloidal particles than the other oxidation states of plutonium. As a result, plutonium can be expected to migrate most rapidly if it is in the pentavalent oxidation state. The total solubility however, is still limited by the formation of the highly insoluble amorphous Pu(OH)₄. Sorption of hydrolyzed Pu(IV) in natural water on mineral surfaces and surfaces coated with organic material is accountable for the very low concentrations of dissolved Pu even in the absence of Pu(OH)₄ (am) or PuO₂ (c). The strong tendency of Pu(OH)₄ to sorb on surfaces is a dominant and often controlling feature in plutonium geochemistry.

The data amassed during AME studies is consistent with the above expectations of plutonium chemistry. The data indicate that plutonium in RFETS surface waters has an extremely low solubility, with concentrations of "soluble" plutonium in the femptomolar (10⁻¹⁵ M) range, similar to global fallout. This extremely small amount of "soluble" plutonium (at femptomolar concentrations) is more consistent with plutonium(V). The data also indicate that the bulk of plutonium is associated with colloidal particles, consistent with plutonium(IV) chemical behavior. Extended X-ray Absorption Fine Structure (EXAFS) studies show unambiguously that plutonium in soils taken from the 903 Pad is plutonium(IV), and in the chemical form of relatively insoluble PuO₂. This is significant in that it had been widely held at the Site that the chemical form was the dioxide, but this had never been proven. The synchrotron radiation studies unequivocally demonstrate that it is indeed PuO₂.

Most probable chemical forms of Pu in RFETS concrete and process waste lines. The source of the plutonium contamination in concrete varies, but can be categorized as either resulting from fires (smoke), or resulting from nitric acid spills inside the buildings. It is likely that any plutonium contamination deposited from fires would be the oxide, PuO₂. In nitric acid process chemical solutions, high acid concentrations are used to prepare Pu(NO₃)₆²⁻ which was used for anion exchange purification. The high acid concentration prevents Pu(IV) hydrolysis. Since concrete is highly basic, and plutonium, particularly Pu(IV) is exceedingly susceptible to hydrolysis and polymerization reactions, neutralization of a nitric acid solution of Pu(IV) will result in almost immediate

generation of the hydrous oxide (or intrinsic colloid) of Pu(IV), often described as $\text{PuO}_2 \cdot 2\text{H}_2\text{O}$. This is also the anticipated result for a nitric acid solution of Pu(IV) being spilled onto soil, where it will ultimately become neutralized and hydrolyze. These hypotheses will be tested this year using synchrotron radiation studies on concrete samples.

The role of aqueous transport calculations at the RFETS Since we anticipate that the chemical form of plutonium in either the soils or in concrete will be relatively insoluble, transport-modeling calculations that assume soluble forms of plutonium are likely to be of little value. Indeed, while we point out that plutonium in soils at RFETS is relatively insoluble, uranium on the other hand can be classified as being slightly soluble. Therefore, uranium will pose a higher probability of aqueous dissolved transport. A thorough understanding of the uranium geochemistry, the uranium source-term, and the overall water balance at the Site are therefore of greater importance with respect to transport calculations.

Pu at RFETS in comparison to reported Pu migration in groundwater at Nevada Test Site At the public meeting, the question was raised about the Kersting et al's publication on migration of Pu in groundwater at the NTS. We point out that the maximum measured concentration of Pu at the ER-20-5 site at NTS was approximately 10^{-14}M (a value close to fallout levels). This value is lower than the solubility limit of Pu(V), and brackets the calculated solubility limits of Pu(IV) which are between $10^{-12} - 10^{-17}\text{M}$. The NTS studies indicate that >99% of the Pu was associated with colloidal particles, though it was not determined whether the Pu was intrinsic radiocolloid, or whether the Pu was associated with colloidal sized clay and zeolite particles in the groundwater. The point of the paper was that transport models that don't include colloid-facilitated transport (ie particulate transport) may underestimate the migration of plutonium. So, what is the similarity to RFETS? First, we have independently recognized (prior to the Nature publication) that particulate transport is not only important, but likely to be the dominant migration process for plutonium at RFETS soils. Further, we note that at NTS, large amounts of plutonium were "injected" 300 meters below the surface by the nuclear detonation. From drill-back operations, we know that approximately 98% of the plutonium is present in the melt-glass that forms in the bottom of the cavity. These melt glasses are extremely radioactive. We also know that extremely high radiation fields will damage the glass (over short time periods), and could conceivably result in the formation of small silicate colloids. In summary for the NTS system, deep subsurface injection via nuclear detonation, encapsulation (perhaps mineralization) of the plutonium in highly radioactive glass, and artificial groundwater gradients imposed via pumping rates result in the detection of particulate (colloidal) plutonium at or near the global fallout level. The situation at RFETS is very different. Plutonium particles are predominantly confined to the top few centimeters of the soil surface. Furthermore, we do not have the extremely high radiation fields associated with

plutonium particles dispersed in the soils at RFETS, and the plutonium is not encased in silicate glass but is in the form of PuO_2 . The extremely high hydrolytic gradients ($0.03 \text{ m}^3/\text{min}$) do not exist at RFETS. So other than the recognition that one must include particulate transport in migration models (the point of the paper), there are very few similarities.

Documents provided to advisory group

Actinide migration evaluation schedule
RSALs report

Documents and information requested for advisory group

Uranium source, berm boring data, and input reports (metals and organics) for solar ponds plume – maybe a data dump for all measurements In borehole soil samples, what contaminants are observed and where

Participants in AMS technical meetings

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12
12